Preparation of Fluorine-doped Tin Oxide by a Spray Pyrolysis Deposition and Its Application to the Fabrication of Dye-sensitized Solar Cell Module

S. Kaneko, S. Kawasaki, P. V. V. Jayaweera and G. R. A. Kumara

SPD Laboratory, Hamamatsu 432-8003, JAPAN

E-mail: skaneko@spdlab.com; URL:http.//www.spdlab.com

Abstract

Spray pyrolysis deposition (SPD) technique has been employed to prepare large area fluorine-doped tin oxide (FTO), nanocrystalline TiO_2 and catalytic Pt films for dye-sensitized solar cell (DSC) module. The transparent conducting FTO film gave low sheet resistance 8 Ω/□ and average visible light transmittance exceeded 80 %. Large area (15 x 15 cm²) DSC module prepared here shows efficiency 7.4 % at AM-1.5 simulated sun light.

I. Introduction

Spray pyrolysis technique is the most suitable process to deposit uniform large area thin film, where a thin film is deposited by spraying a starting solution on heated surface and then constituents react to form a new solid phase(Fig.1).[1] This technique is particularly useful for the deposition of oxides and has long been production method for applying a transparent conducting tin oxide to glass substrate.

Fluorine doped tin oxide (FTO)[2] has been recognized as a very promising material for a number of optoelectronic applications, because it is quite stable for atmospheric conditions, chemically inert, mechanically hard, high-temperature resistant, etc.

SPD technique(Fig. 1,2) has been applied here to prepare FTO, TiO_2 and Pt coated titanium counter electrode used for DSC[3] module fabrication. Large area (15 x 15 cm²) dye-sensitized solar cell[4,5] module was constructed with these materials (Fig. 3-5) and its photovoltaic properties were evaluated.

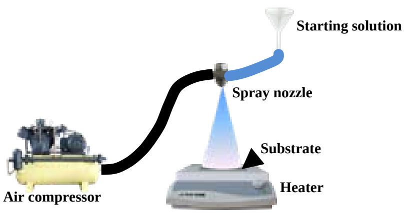

Fig 1. Schematic diagram of SPD

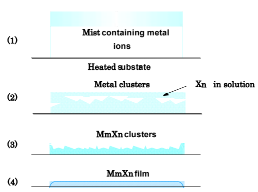

Fig 2. Film formation process

II. Experimental

Preparation of FTO and TiO_2 colloid[4]

Dibutyltin Diacetate (DBTDA) was dissolved in ethanol. NH_4F was dissolved in water. These two solutions were mixed and agitated ultrasonically for 30 min. This mixture was sprayed onto a heated glass plate (surface temperature = 470 °C) using KM-150 SPD machine (Fig. 3) until the film thickness reached to 800 nm. Silver grids were coated on FTO using a mini robot machine at r.t. The plate was sintered at three steps, (1) 150 °C for 10 min. (2) 350 °C for 10 min and (3) 500 °C for 10 min in air.

Fig 3. Outside view of SPD machine, KM-150

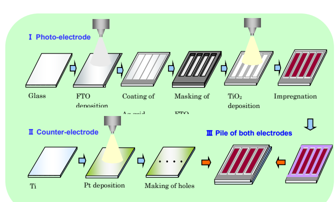

Fig 4. Fabrication processes of DSC module

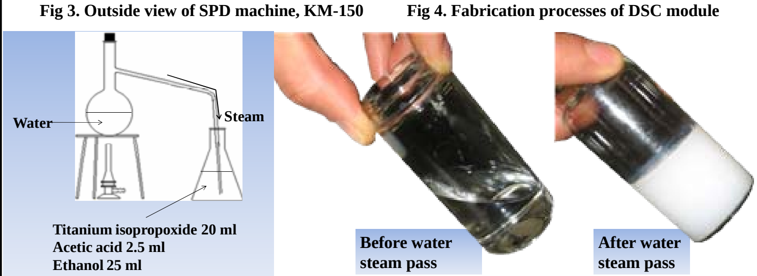

Fig 5. Preparation of TiO_2 colloid

Titanium isopropoxide (20 ml) and Acetic acid (2.5 ml) were mixed with 25 ml ethanol. And steam was passed through the solution. Rapid hydrolysis of titanium isopropoxide and the expulsion of ethanol by steam produced a transparent TiO_2 colloids. Above TiO_2 colloids were ground with 50 ml of water in a mortar and autoclaved at 150 °C for 3 h.

TiO_2 coating[5]

Autoclaved solution (20 ml), 5.5 ml of acetic acid, 20 ml of ethanol and 5 drops of Triton-X-100 were mixed and sonicated ultrasonically for 10 min. This solution was sprayed to heated Ag grids coated FTO glass plate (temperature 160 °C) with KM-150 SPD machine until the film thickness reached about 12 μm. This plate was sintered at 450°C for 30 min in air and allowed to cool gradually. The plate is soaked in a 3 x 10^{-3} M dye solution [Ruthenium-719 in acetonitrile + tert-butyl alcohol (1 : 1)] at r. t. for overnight.

Preparation of titanium counter electrode and DSC module fabrication

Holes were pierced in Ti plate (15 x 15 cm²) and heated to 130 C. Ethanol solution containing chloroplatinic acid was sprayed to heated Ti metal plate by KM-150 SPD machine and sintered at 450 °C for 10 min. UV hardening sealant was coated on Ag grids and the Pt coated Ti counter electrode was pressed on the dye coated TiO_2 electrode. UV light was irradiate for 30s to harden the sealant. The electrolyte (0.1 M LiI, 0.05 M Iodine, 0.5 M 4-tert-butylpyridine, and 0.6 M dimethyl-propyl imdazolium iodide in acetonitrile) was injected into the cell through the holes. Figure 4 shows a summarized DSC fabrication processes.

III. Results

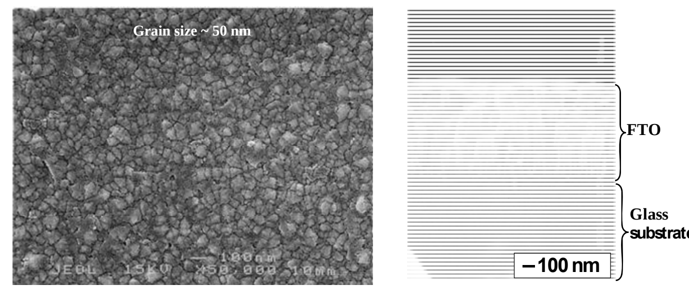

Fig. 6. SEM Photographs of FTO (Thickness ~800 nm)

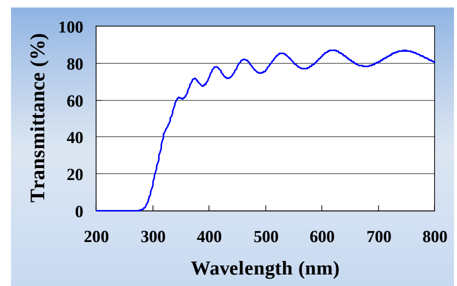

Fig. 7. Transmittance spectrum of FTO

Table 1. Physical Properties of FTO

Film thickness (nm)	Sheet resistance (Ω/□)	Carrier concentration (cm⁻³)	Mobility (cm²/Vs)	Resistivity (Ωcm)	Transmittance (%)
800	6	5.75×10^{20}	38.4	2.83×10^{-4}	80

Principles of operation of dye-sensitized solar cell

Photo-excitation dye molicules inject electron into the conduction band of the TiO_2. The dye molecule is regenerated by the redox system, which itself is regenerated at the counter electrode by electrons passed through the load. The open-circuit voltage of the DSC corresponds to the difference between the redox potential of the mediator and the Fermi level of the TiO_2.

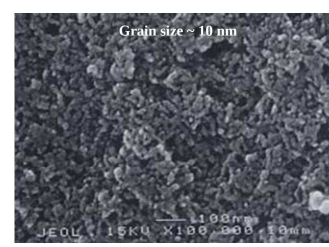

Fig 8. Surface morphology of TiO_2 coated

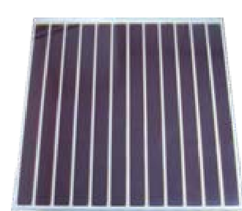

Fig. 9. Outside view of DSC module (15 × 15 cm²)

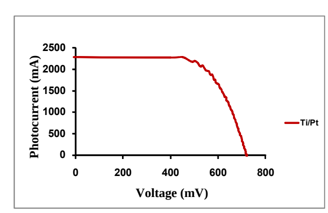

Fig. 10. I-V characteristic of DSC module (15 × 15 cm²)

Table 2. DSC module properties

Jsc (mA/cm²)	Isc (A)	Voc (mV)	FF	η (%)
15.1	2.5	720	0.68	7.4

IV. Conclusions

- ❑Highly transparent and conducting FTO was successfully prepared by a SPD technique. Our FTO film gave low sheet resistance 8 Ω/□ and average transmittance in the visible light region exceeded 80 %.
- ❑High efficient large-area DSC module was constructed with this high performance FTO: The highest efficiency obtained was 7.4% with Ti counter electrode for the cell of 15 × 15 cm² at AM-1.5 simulated sun light.

References

1. I. Yagi, and S. Kaneko, *Chem. Lett.*, 1992, 2345-48.
2. S. Kaneko *et al.*, *Ceram. Trans.*, 1998, 100,165-74.
3. B. O'Regan, and M. Gratzel, *Nature*, 1991, 353, 727.
4. M. Okuya *et al.*, *J. Photochem. Photobiol.*, 2004, 164, 167-72.
5. G. R. A. Kumara *et al.*, *Prog. Photovolt: Res. Appl.;* 2006, 14, 643-651.

ICCG 8th, June 13-17, 2010, Braunschweig, Germany